

(19)



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European Patent Office
Office européen des brevets



(11)

EP 0 774 450 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
09.02.2000 Bulletin 2000/06

(51) Int Cl.7: **C07C 17/15, C07C 17/152,**
C07C 17/154, C07C 17/156,
C07C 17/158

(21) Application number: **96118115.3**

(22) Date of filing: **12.11.1996**

(54) **Method for reducing formation of polychlorinated aromatic compounds during oxychlorination of C1-C3 hydrocarbons**

Verfahren zur Reduzierung der Bildung von polychlorierten aromatischen Verbindungen während der Oxychlorierung von C1-C3 Kohlenwasserstoffen

Procédé pour réduire la formation de composés polychlorés aromatiques lors de l'oxychloration d'hydrocarbures C1-C3

(84) Designated Contracting States:
**AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE**

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(30) Priority: **17.11.1995 US 559123**

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(43) Date of publication of application:
21.05.1997 Bulletin 1997/21

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BE-A- 680 413 DE-B- 2 556 521
US-A- 3 192 128

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Description

[0001] The present invention relates to processes involving oxychlorination of C₁-C₃ hydrocarbons especially methane, ethane, propane, ethylene, propylene, acetylene, and propyne using hydrogen chloride from sources other than the thermal cracking of the product from the operated oxychlorination process.

BACKGROUND OF THE INVENTION

[0002] The recent literature concerning the commercial use of chlorine has focused on the small but measurable quantities of polychlorinated aromatic compounds such as chlorobenzenes, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) all of which are hereinafter referred to as PCDD/F(s) and are considered environmentally toxic. These highly undesirable compounds (HUCs) are found in soil and lake sediments and their reduction or elimination from industrial production is becoming of paramount concern. The literature contains many references to PCDD/F formation which in general support the position that the formation of trace quantities of PCDD/F's is unavoidable in many industrial chlorine containing processes involving addition or removal of chlorine atoms from non-aromatic hydrocarbons. This is particularly true for oxychlorination processes, and especially true for the oxychlorination of ethylene to 1,2-dichloroethane, also referred to as ethylene dichloride (EDC), an important intermediate in the production of vinyl chloride monomer (VCM).

[0003] Because of the concerns about the toxicity and bioaccumulation of polychlorinated aromatics, minute quantities are being monitored in a variety of industries, including solid waste incinerators, EDC/VCM processes and other processes that involve the chlorination, oxychlorination or hydrochlorination of non-aromatic hydrocarbons, including the reverse processes, i.e. dechlorination or dehydrochlorination. A recent report compiled from case studies of emissions from EDC/VCM processes in Europe estimates annual emissions of what are referred to as toxic equivalents of 2,3,7,8-tetrachloro dibenzodioxin (TCDD) at 1.8 kg. See De Vorming van PCDFs, PCDDs en Gerelateerde Verbindingen Bij de Oxychlorination van Etheen, Evers, E.H.G., Dept. of Environmental Toxicology, University of Amsterdam, Contract No. ZH4005, Nat. Water Service District of So. Holland (hereinafter referred to as the NWS Study) 1989. MTC Pub. No. MTC89EE. Moreover, experts are in disagreement over what levels of these toxins are generated from both natural and industrial processes.

[0004] There are numerous literature citations of investigations concerning the various synthetic routes giving rise to PCDD/Fs. Chemosphere, Vol. 23, Nos. 8-10, O. Hutzinger, Editor, Pergamon Press, 1991. By way of summary, the significant precursors that may lead to the formation of PCDD/Fs noted in the literature include chlorophenol, benzene, chlorinated benzene, and diphenyl ether. These species have been found to convert to PCDD/Fs via condensation, free-radical and ionic mechanisms. Chlorinated Dioxins and Related Compounds, O. Hutzinger, et. al, Editors, Pergamon Press, 1982.

[0005] The *de novo* synthesis of PCB's and PCDD/Fs from non-aromatic precursors (including elemental forms) has been reported in the literature for oxychlorination processes. Chemosphere, Eklund, G.; Pederson, J.R.; Stromberg, B., 17, 575, 1988. The NWS study demonstrated that a number of PCDD/Fs were detected in the gas phase and catalyst residue of a simulated oxychlorination process. The total amount of PCDD/F's observed in the NWS experiments was 546 nanograms per 1.31 grams of EDC formed or 417 ng/g (ppb). The PCDD/Fs congener pattern formed in the NWS experiments was very similar to that found in the waste sludge of the VCM industries along the Rhine river basin and indicates that the laboratory study accurately modeled the process occurring in commercial units. The authors of the NWS Study concluded that copper catalyst plays a role in formation of PCDD/Fs in mediums in which carbon, chlorine, oxygen and active catalytic surfaces are present. The data generated appear to confirm conclusions of other researchers that PCDD/Fs are formed *de novo* in the oxychlorination of alkanes and alkenes and especially with oxychlorination of ethylene to form EDC. The term *de novo* is defined as formation of PCDD/Fs directly from acyclic, aliphatic hydrocarbon, such as methane and ethylene, in the presence of oxygen and HCl. The researchers presumed that aromatization of simple carbon structures was occurring in order to account for the apparent *de novo* synthesis.

[0006] *De novo* formation of chlorinated alkenes, benzenes,-phenols and biphenyl has also been reported to be formed by the reaction of CO₂ and HCl in the presence of catalysts. Chemosphere, Stromberg, B. 27, 179, 1993; Chemosphere, 23, 1515, 1990. These catalysts include many commercially used materials like those used in oxychlorination processes. In addition, fly ash from municipal solid waste incinerators has also been shown to catalyze formation of PCDD/Fs. a) Chemosphere, Ross, B.J.; Naikwadi, K.P.; Karasek, F.W., 19,291, 1989; b) Chemosphere, Benfenati, E.; Mariani, G.; Fanelli, R.; Zuccotti, S., 22, 1045, 1992; and Chemosphere, Born J.G.P.; Louw, R.; Mulder, P., 26, 2087, 1993. One such study has shown that favorable conditions occur at temperatures between 280°C and 300°C, leading to a consensus among investigators of incineration methods that PCDD/Fs likely form in the post-combustion vent gas cooling zones of solid waste incinerators. Thus, studies have shown that *de novo* synthesis of chlorinated aromatic compounds apparently occurs under a variety of conditions.

[0007] With the many reports of *de novo* formation of PCDD/Fs in industrial chlorine consuming processes, reduction

or elimination of these by-products is highly sought. Some approaches have focused on improving the reaction selectivity to making the desired product. For example, one approach which is considered from the standpoint of reduction in the level of byproducts produced in the manufacture of EDC, is the improved direct chlorination process disclosed in US Patent Number 4,410,747 ('747). This liquid phase reaction of ethylene and chlorine as taught in '747 is conducted at the boiling point of the EDC liquid in the presence of a metal chloride catalyst and added aromatic hydrocarbon, such as benzene. The side reactions forming undesired by-products, principally 1,1,2-trichloroethane, are reduced. Following the view that *de novo* synthesis of PCDD/F's is occurring, improved reaction selectivity could reduce the level of *de novo* PCDD/F's formed.

[0008] Other improvements have focused on reduction in the volume of effluent discharged from the oxychlorination process. In the balanced process for oxychlorination of ethylene to make EDC, there is provided the recapture and reuse of hydrogen chloride from the cracking of 1,2-dichloroethane to vinyl chloride monomer. The amount of waste effluent is reduced considerably in the re-use of HCl. This recycled HCl is referred to herein as "internally sourced" and this internally sourced HCl is typically separated from EDC, VCM and byproducts by distillation.

[0009] Recent developments in the world-wide chemical industry are leading to a shift in the manufacturing of VCM away from the balanced VCM process, and towards the increasing use of HCl from external, i.e., non-oxychlorination processes. The present invention is concerned with the use of this "external" HCl, i.e., from sources other than that obtained in separating HCl from the effluent generated in the thermal cracking of the oxychlorination product, e.g., EDC. External HCl is produced in industrial processes such waste incineration of chlorinated materials; the manufacture of organic isocyanates; high temperature chlorinolysis of C₁-C₃ hydrocarbons; and the dehydrochlorination of chlorinated materials such as chlorine containing polymers, chlorinated hydrocarbons, chloroacetic acid, CFC's, HCFC's and other industrially useful materials.

SUMMARY OF THE INVENTION

[0010] In accordance with the invention there is provided an operated oxychlorination process for manufacturing chlorinated hydrocarbon. The process involves fixed bed or fluid bed catalyzed oxychlorination of a hydrocarbon reactant containing from 1 to 3 carbon atoms. The oxychlorination process comprises contacting a C₁ - C₃ hydrocarbon reactant with oxygen or oxygenated gas and HCl, wherein at least a portion of the hydrogen chloride to be consumed is obtained from an external source other than from recovery of hydrogen chloride from the thermal pyrolysis of the product of the operated oxychlorination process. The feedstocks are reacted in the presence of the oxychlorination catalyst in a heated reaction zone operated at from 150°C to 600°C wherein chlorinated hydrocarbon product is recovered from the effluents of the reaction zone. The process is characterised by the fact that HCl is pretreated before use in the operated oxychlorination process by a means for removal of the aromatic hydrocarbons.

DETAILED DESCRIPTION

[0011] The present invention stems from the unexpected discovery that the *de novo* synthesis of PCDD/Fs is not a necessary result in oxychlorination of non-aromatic hydrocarbons under industrially practiced conditions. In carefully controlled quantitative experiments, a laboratory oxychlorination process was monitored starting with externally sourced HCl, ethylene and air or oxygen in the presence of a copper catalyst. There was observed, in agreement with the literature, measurable quantities of PCBs and PCDD/Fs. The measured levels of PCB's and PCDD/Fs observed in the effluent from oxychlorination was surprisingly reduced after external HCl was first treated for the removal of aromatic hydrocarbons. It has thus been shown that a major amount of PCDD/F's found in the effluent of the oxychlorination process is contributed not by *de novo* synthesis during the oxychlorination of aliphatic hydrocarbon but from a low level of aromatic compounds discovered in external HCl feedstock. It has now also been shown that these aromatic compounds can be removed by conventional means, prior to usage of the HCl in the oxychlorination process, thus preventing their conversion to PCB's and PCDD/Fs during oxychlorination.

[0012] The present invention provides an improved oxychlorination process for converting aliphatic hydrocarbon to chlorinated aliphatic hydrocarbon having reduced levels of PCB's and PCDD/Fs including contacting an oxychlorination catalyst with an aliphatic hydrocarbon reactant, an oxygen containing gas and some or all of the chlorine source from external hydrogen chloride in a heated reaction zone operating at from 150°C to 600°C, the preferred temperature depending on the specific hydrocarbon feedstock, and recovering chlorinated aliphatic hydrocarbon from the effluents of the reaction zone, the improvement consisting of the use of external (non-cracking grade) HCl which has been pre-treated with a means for removal of aromatic compounds. Suitable means for the removal of aromatic compounds from hydrogen chloride include multistage fractional distillation, adsorption, absorption, and reaction processes.

[0013] Removal of aromatic compounds from hydrogen chloride by distillation includes the steps of vaporizing HCl in a vessel equipped with a reflux condenser, followed by collecting condensed vapors practically free of higher or lower boiling compounds. The vaporizing and condensing steps preferably include a means for providing a counter-

current, multistage fractionation as is widely used in distilling a variety of liquids.

[0014] Another means for removing aromatic compounds from externally sourced HCl involves the step of passing HCl through a vessel containing solid or liquid adsorbent or absorbent. Solid adsorbents are known and used in the art and include, but are not limited to, activated carbon, zeolite, alumina, diatomaceous earth, various forms of silica such as silica gel; and supported, selective adsorbing or absorbing polymer resin. Liquid absorbents include but are not limited to paraffins, e.g. aliphatic hydrocarbons such as pentanes, hexanes, C₅-C₉ distillate fractions, and the like, and water.

[0015] Removal of aromatic compounds from external HCl can also be accomplished by hydrogenation reactions which includes the treatment by an hydrogenation metal catalyst such as nickel, platinum or palladium in the presence of a hydrogen source to convert the aromatic compounds to saturated cyclic aliphatic compounds. Catalytic oxidation over an oxidation catalyst in the presence of oxygen to convert the aromatic compounds to carbon dioxide and water is another reaction process which can be used to remove aromatic compounds from HCl.

[0016] The particular method of removing aromatic compounds from HCl is not critical and may be chosen by the practitioner merely on the basis of available equipment and preferred economics which are beyond the scope of this disclosure. Among the pretreatment steps available, preferred methods include treatment with an oxidation catalyst, passing HCl through an adsorbing column containing activated carbon, and extraction with paraffin liquids.

[0017] In another aspect of the invention, there is provided an improved oxychlorination process effluent which contains reduced, and preferably less than a detectable level of polychlorinated aromatics, the effluent is produced in an oxychlorination process by contacting with an oxychlorination catalyst in a heated reaction zone operating at from 150°C to 600°C, a C₁ to C₃ hydrocarbon reactant, such as methane, ethane, ethylene, propane, propylene, acetylene, chloroethane, chloropropene, dichloromethane, dichloroethane, and the like, in the presence of an oxygen containing gas such as air, and hydrogen chloride, whereby a portion or all of the chlorine is provided by externally sourced hydrogen chloride, that is, the HCl is obtained from a source outside the recovery portion of the aliphatic hydrocarbon oxychlorination process itself. Internally sourced HCl is obtained by thermal cracking of the intermediate chlorinated hydrocarbon from that process. Therefore, in the present invention at least a portion of the HCl used must be obtained from a process other than the thermal cracking of an intermediate chlorinated aliphatic hydrocarbon from the operated oxychlorination process. In the present invention the externally sourced hydrogen chloride used must be pre-treated with a means for the removal of aromatic compounds prior to entry to the heated oxychlorination reaction zone.

[0018] Suitable catalysts used in the oxychlorination process are known and understood conventionally. Examples are disclosed in U.S. Patent Nos. 3,624,170, 4,446,249, 4,740,642, and 5,011,808 and European Patent Publication No. 0255156. The process conditions required in catalytic oxychlorination are also known and established in the art. Examples are described in U.S. Patent No. 3,488,398 to Harpring *et al.* Oxychlorination catalysts are suitable either in the form of fixed bed types or fluid bed types.

[0019] In the case of oxychlorination of saturated hydrocarbons containing 1, 2 or 3 carbon atoms the heated reaction zone is operated generally from 300°C to 600°C. In the case of oxychlorination of unsaturated hydrocarbons containing 2 or 3 carbon atoms, the heated reaction zone is operated from 150°C to 300°C. Halogenated derivatives can also be advantageously chlorinated using the present process and include chloromethane, dichloromethane, chloroethane, dichloroethane, trichloroethane, fluoromethane, fluoroethane, fluoropropene, chlorofluoromethane, chlorofluoroethane, chlorofluoropropane, and bromo-substituted C₁ - C₃ hydrocarbons. The process is operated at atmospheric pressure or above atmospheric pressure. The molar ratios of reactant feed gases HCl/C₂H₄/O₂ are generally maintained at 2/1-1.5/0.5-1.0. The process can be operated as a once through method without reuse of unreacted feed gases or the process can be operated by recycling of unreacted feed gases. Further treatment of the chlorinated product is possible using conventional thermal cracking and/or purification means established in the art.

45 Experiments

[0020] Several experiments were performed to demonstrate that the careful removal of aromatic compounds from HCl streams used as feedstocks to oxychlorination processes will lead to a significant reduction in the amount of PCBs and PCDD/Fs.

[0021] Reactions were performed in laboratory scale fluid-bed oxychlorination reactors operated between 210°C and 245°C, contact time of from 15 and 40 seconds and otherwise, within the operating range of commercial units. Contact time is defined as the fluidized bed volume of the catalyst bed divided by the volumetric flow rate of the sum of all the feed gases at reactor control temperature and reactor top pressure. In some experiments, previously measured levels of aromatic compounds were allowed to enter the reactor with the feed gases. Other experiments involved the artificial addition of benzene, dichlorobenzene, or toluene as model compounds. Baseline control experiments were performed wherein no aromatic compounds were present in the feed or on the catalyst.

[0022] It is reported in the scientific literature dealing with quantitative analysis of PCBs and PCDD/Fs that the PCBs and particularly PCDD/Fs formed in oxychlorination and other processes accumulate and become concentrated on

the catalyst and are found in residues extractable from the solid catalyst particles. De Vorming van PCDFs, PCDDs en Gerelateerde Verbindingen Bij de Oxychlorination van Etheen, Evers, E.H.G., Doctoral Thesis, University of Amsterdam, 1989. MTC Pub. No. MTC89EE. In the experimental work which is summarized below, analyses were performed on both the reactor effluent (product and gases) and the solid catalyst particles. For analytical consistency and simplicity, only results of analyses on reduces from catalyst samples are reported below.

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Oxychlorination Test Conditions.

[0023] A locally built, lab scale fluidized bed reactor was employed. Approximately 300g of catalyst was charged and controlled to temperature between 210°C and 245°C by means of resistance heating. The system was operated at atmospheric pressure. The feed gases C₂H₄, HCl and air or N₂ and O₂ were introduced to the reactor just below the catalyst bed. Feed rates were maintained using commercial mass flow controllers such that the fluidized bed contact time was approximately 25 seconds and the HCl/C₂H₄/O₂ molar feed ratio was approximately 1.96/1.0/1, respectively.

[0024] The reactants and products pass upwards through the fluidized bed to a disengagement zone which separates the catalyst particles from the product gases. The product gases are then transported through an enclosed system to liquid and gas sampling stations. When analyses were to be made it was essential that the reactor and all downstream sample lines were maintained above the dew point of the gases.

[0025] Catalyst samples were removed from the reactor during reaction conditions. A sample port located near the bottom of the reactor but above the point where the feed gases are introduced was opened and the catalyst sample taken into a clear glass vial and sealed.

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[0026] The catalyst samples were extracted with toluene according to the following procedure:

[0027] Five grams of catalyst was placed in a 50cc crimp vial. Toluene (25ml) was added and the sample mechanically shaken for 7 hours and then allowed to stand for approximately 15 hours. The catalyst and solvent was filtered through #2 Whatman paper into a 6 dram amber vial. 2,4,8-Trichlorodibenzodioxin was added as an internal recovery standard.

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The sample was then evaporated to dryness. The residue was reconstituted in 2-3ml isoctane, transferred to a 4ml amber vial, and evaporated to dryness without heating. The residue was then extracted in 0.1 ml isoctane for analysis by GC.

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[0028] Two methods of analysis by GC were employed. Qualitative screening was performed on an HP5890 series II GC equipped with an electron capture detector (ECD) and RTX-5 column. Quantitative analysis were performed on an HP5870 GC equipped with an HP 5790 mass selective detector and a 30m XTI-5 capillary column (0.25µm film).

Sample size was 2 µl, and the column conditions were 70°C for two minutes, 15°C/minute ramp to 300°C, and a soak time of 17.7 minutes. Detection limits were to 0.1 ng PCBs or PCDD/Fs per gram of catalyst removed from the reactor.

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[0029] Quantitative data reported below are listed in units of ng/g on the catalyst. Values for PCBs with 8, 9, and 10 chlorine atoms are summed and reported as "PCBs". Under the heading "OCDD" and "OCDF" are the octachlorinated dibenzodioxins and octachlorinated dibenzofurans respectively. It is widely known in the art that the oxychlorination process favors the formation of the more highly chlorinated PCDFs, and thus less toxic, derivatives over the lower chlorinated, and more environmentally suspect congeners.

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[0030] Experiments were conducted on fresh catalyst, with catalyst previously used in the laboratory oxychlorination reactor, and with catalyst previously used in the laboratory oxychlorination reactor in the presence of added aromatic hydrocarbons and chlorinated aromatic hydrocarbons.

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[0031] Experiments were also performed to determine if chlorinated ethene derivatives would lead to aromatic compounds or their known precursors (derivatives of butadiene). In all cases, no evidence was found for the aromatization of C₂ hydrocarbons or for the production of PCBs or PCDD/Fs when the feed to the reactor contained only C₂H₄, HCl, O₂ and N₂.

Example 1 Fresh Catalyst (baseline)

[0032] A sample of a fresh oxychlorination catalyst of the type disclosed in US 5,292,703 was extracted as outlined above. Qualitative and quantitative GC analysis indicated that fresh catalyst contained only minute levels of PCBs and

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PCDD/Fs. The levels of contamination found were in agreement with those reported in the literature. They are similar to the background levels found on a wide variety of commercial and non-commercial materials.

[0033] This analysis was repeated on 5 additional samples of fresh catalyst to establish a baseline. The results are summarized in Table 1 below. Units are listed in nanograms per gram of EDC produced (ng/g).

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TABLE 1

Catalyst	PCBs ng/g	OCDD(ng/g)	OCDF(ng/g)
1-A	<0.1	non-detected	~0.8

TABLE 1 (continued)

Catalyst	PCBs ng/g	OCDD(ng/g)	OCDF(ng/g)
1-B	<5	non-detected	<5
1-C	3.0	non-detected	2.3
1-D	<1	non-detected	<1
1-E	<1	non-detected	<1
1-F	<1	non-detected	<1

Example 2

[0034] A sample of fresh catalyst was used in the laboratory oxychlorination reactor operating at 225°C, with molar ratios of HCl/C₂H₄/O₂ controlled at 1.97/1.0/1.1, and with approximately 25 seconds of contact time. The HCl, ethylene, and air were quantitatively pre-treated for the removal of aromatic compounds. The catalyst was sampled and extracted as described above. Surprisingly, no evidence was found for elevated levels (compared to baseline experiments) of PCBs or PCDD/Fs on quantitative analysis of the catalyst particles. If unavoidable, *de novo* synthesis of polychlorinated aromatics was occurring, there would have been observed easily detectable increases in PCBs and/or PCDD/Fs on the catalyst particles. Therefore, with no aromatic compounds present in the HCl after treatment using a suitable means for eliminating aromatic compounds, the oxychlorination effluent will contain reduced levels of PCBs and PCDD/Fs.

Example 3

[0035] The fresh catalyst was placed in the laboratory oxychlorination reactor at the above conditions. A mixture of aromatic hydrocarbons consisting mainly of xylenes and C₃-benzenes was introduced at a combined level of approximately 200 ppb based on the HCl feed rate. The reaction was conducted for approximately 24 hours to allow for a steady-state to be established, and the catalyst was sampled and analyzed as described above. GC-MSD results indicated elevated levels of PCBs and PCDD/Fs: PCBs=21.2 ng/g; OCDD=non-detected; OCDF=94.2 ng/g. In a similar experiment we found PCBs=23.9 ng/g; OCDD=non-detected; OCDF=14.6 ng/g. These observations illustrate that aromatic compounds present in the HCl stream do contribute to the amount of polychlorinated aromatics found in the oxychlorination effluent.

Example 4

[0036] Following the same procedure as in Example 3, benzene was introduced at a rate of approximately 14% of the HCl feed rate for 6 hours. The catalyst was sampled and analyzed as described above, and elevated levels of PCBs and PCDD/Fs were found: PCBs=5.3 ng/g; OCDD= not analyzed; OCDF=1137 ng/g.

Example 5

[0037] Following the procedures for Example 4 above, toluene was introduced at a rate of approximately 4% based on the HCl feed. Analysis of the catalyst after about 6 hours of exposure gave the following results: PCBs=46.4 ng/g; OCDD=42.3 ng/g; OCDF=315.6 ng/g.

Example 6

[0038] In an effort to determine if chlorocarbons can join to form butadiene and butadiene derivatives which are known to react with olefins to yield aromatic compounds, perchloroethylene was introduced to the laboratory oxychlorination reactor operating under conditions similar to those in Example 5. Qualitative analysis of the reaction product by GC-MSD indicated the presence of all the chlorinated derivatives of ethane and ethene. However, no evidence was found for C₃, C₄, or higher hydrocarbons or their derivatives. This indicates that there is no aromatization occurring under typical oxychlorination conditions. The catalyst type used in the above experiments is not unique in regard to the observed behavior and is merely illustrative of a typical oxychlorination catalyst in commercial use.

DISCUSSION

[0039] Example 1 illustrated that before usage in an oxychlorination reaction, fresh catalyst is seen to contain only trace quantities of PCBs and PCDD/Fs . Example 2 illustrated the surprising result that when all feed components used

in the process are free of aromatic compounds and fresh catalyst is used, there is no *de novo* synthesis of PCBs and PCDD/Fs under the conditions which are suitable for industrial scale operation. There are advantages in preventing the formation of PCBs and PCDD/Fs from occurring in the oxychlorination process effluent since the heavy ends by-products contained in the crude EDC and the waste water sludge accumulated from the process can now approach or achieve zero levels of PCBs and PCDD/Fs. There are considerable economic advantages of eliminating the steps of decontamination of the waste effluents. Environmental contamination ultimately is reduced.

[0040] In light of the above understanding, one can appreciate the application of the invention to other similar processes such as chlorination, hydrochlorination, and the reverse processes. The ability for prevention of formation of PCBs and PCDD/Fs can be realized for any industrial process involving chlorine, hydrogen chloride and aliphatic hydrocarbons, under conditions that prevent the conversion of aliphatic hydrocarbons to aromatic hydrocarbons. The present invention is not applicable to those processes where *de novo* synthesis of aromatic and polychlorinated aromatic compounds intrinsically occurs or where aromatic compounds are an integral part of the process.

15 Claims

1. A process for manufacturing chlorinated hydrocarbon with reduced formation of chlorobenzenes, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), said process starting with C₁ to C₃ hydrocarbon reactant selected from the group consisting of methane, ethane, ethylene, acetylene, propane, propylene, methylacetylene, and halogen substituted versions thereof, said process comprising: contacting said reactant with oxygen or oxygenated gas and hydrogen chloride, wherein at least a portion of the hydrogen chloride to be consumed is obtained from an external source other than from recovery from the thermal cracking of the product produced in said oxychlorination process, said contacting is conducted in the presence of an oxychlorination catalyst in a heated reaction zone operating at from 150°C to 600°C wherein chlorinated hydrocarbon is recovered from the effluents of the reaction zone, the process is characterized by the fact that the hydrogen chloride is pretreated with a means for removal of the aromatic hydrocarbons.
2. The process of claim 1 wherein said means for removal of aromatic compounds from said hydrogen chloride is selected from the group consisting of distillation, adsorption, absorption, hydrogenation, and oxidation.
3. The process of claim 1 wherein said means for removal of aromatic compounds is selected from the group consisting of
 - (a) passing said hydrogen chloride through a vessel containing activated carbon,
 - (b) treating said hydrogen chloride with activated charcoal,
 - (c) treating said hydrogen chloride with silica,
 - (d) treating said hydrogen chloride with an aromatic compound adsorptive resin,
 - (e) subjecting said hydrogen chloride to a hydrogenation process,
 - (f) extraction with aliphatic liquid hydrocarbon, and
 - (g) subjecting said hydrogen chloride to an oxidation process.
4. The process of claim 1 wherein said hydrocarbon is selected from the group consisting of methane, ethane and propane and wherein said heated reaction zone is operated at from 300°C to 600°C.
- 45 5. The process of claim 1 wherein said hydrocarbon is selected from the group consisting of ethylene, acetylene, propylene, and methylacetylene and wherein said heated reaction zone is operated at from 150°C to 300°C.
6. The process of claim 1 wherein said hydrocarbon is ethylene.

50 Patentansprüche

1. Verfahren zur Herstellung eines chlorierten Kohlenwasserstoffs unter reduzierter Bildung von Chlorbenzolen, polychlorierten Biphenylen (PCBs), polychlorierten Dibenzodioxinen (PCDDs) und polychlorierten Dibenzofuranen (PCDFs), wobei das Verfahren von einem C₁- bis C₃-Kohlenwasserstoff-Reaktant, der aus der Gruppe ausgewählt ist, bestehend aus Methan, Ethan, Ethylen, Acetylen, Propan, Propylen, Methylacetylen und Halogen-substituierten Derivaten derselben, ausgeht und das In-Kontakt-Bringen des Reaktanten mit Sauerstoff oder sauerstoffangereichertem Gas und Chlorwasserstoff umfaßt, worin wenigstens ein Teil des zu verbrauchenden Chlorwasser-

stoffs von einer externen Quelle erhalten wird, die von derjenigen der Gewinnung durch das thermische Cracken des in diesem Oxychlorierungsverfahren hergestellten Produkts verschieden ist, wobei das In-Kontakt-Bringen in Gegenwart eines Oxychlorierungs-Katalysators in einer erwärmten, bei 150 bis 600 °C arbeitenden Reaktionszone durchgeführt wird, der chlorierte Kohlenwasserstoff aus dem aus der Reaktionszone Austretenden gewonnen wird und das Verfahren durch die Tatsache gekennzeichnet ist, daß der Chlorwasserstoff mit einem Mittel zum Entfernen aromatischer Kohlenwasserstoffe vorbehandelt wird.

2. Verfahren gemäß Anspruch 1, worin das Mittel zum Entfernen aromatischer Verbindungen aus dem Chlorwasserstoff aus der aus Destillation, Adsorption, Absorption, Hydrierung und Oxidation bestehenden Gruppe ausgewählt ist.
3. Verfahren gemäß Anspruch 1, worin das Mittel zum Entfernen aromatischer Verbindungen aus der Gruppe ausgewählt ist, bestehend aus:
 - (a) dem Hindurchführen des Chlorwasserstoffs durch ein Gefäß, das Aktivkohle enthält;
 - (b) der Behandlung des Chlorwasserstoffs mit aktivierter Holzkohle,
 - (c) der Behandlung des Chlorwasserstoffs mit Siliciumdioxid,
 - (d) der Behandlung des Chlorwasserstoffs mit einem Harz, das eine aromatische Verbindung adsorbiert,
 - (e) des Durchführens eines Hydrierungsverfahrens mit dem Chlorwasserstoff,
 - (f) der Extraktion mit einem aliphatischen, flüssigen Kohlenwasserstoff, und
 - (g) des Durchführens eines Oxidationsverfahrens mit dem Chlorwasserstoff.
4. Verfahren gemäß Anspruch 1, worin der Kohlenwasserstoff aus der aus Methan, Ethan und Propan bestehenden Gruppe ausgewählt ist und die erwärmte Reaktionszone bei 300 bis 600 °C betrieben wird.
5. Verfahren gemäß Anspruch 1, worin der Kohlenwasserstoff aus der aus Ethylen, Acetylen, Propylen und Methylacetylen bestehenden Gruppe ausgewählt ist und die erwärmte Reaktionszone bei 150 bis 300 °C betrieben wird.
6. Verfahren gemäß Anspruch 1, worin der Kohlenwasserstoff Ethylen ist.

Revendications

1. Procédé amélioré de fabrication d'un hydrocarbure chloré avec formation réduite de chlorobenzènes, de biphenyles polychlorés (PCB), de dibenzodioxines polychlorées (PCDD) et de dibenzofurannes polychlorés (PCDF), ledit procédé partant d'un réactif hydrocarbure en C₁-C₃ choisi dans le groupe constitué par le méthane, l'éthane, l'éthylène, l'acétylène, le propane, le propylène, le méthylacétyle, et leurs versions halogénées, ledit procédé comprenant: la mise en contact dudit réactif avec de l'air ou de l'air enrichi en oxygène et du chlorure d'hydrogène, ladite mise en contact étant réalisée en présence d'un catalyseur d'oxychloration au cuivre (II) dans une zone réactionnelle chauffée fonctionnant à une température de 150°C à 600°C, dans lequel l'hydrocarbure chloré est récupéré dans les effluents de la zone réactionnelle, le procédé étant caractérisé par le fait que l'air est prétraité par un moyen d'élimination des hydrocarbures aromatiques.
2. Procédé selon la revendication 1, dans lequel ledit moyen d'élimination des composés aromatiques de l'air est choisi dans le groupe constitué par la distillation, l'adsorption, l'absorption, l'hydrogénéation et l'oxydation.
3. Procédé selon la revendication 1, dans lequel ledit moyen d'élimination des composés aromatiques est choisi dans le groupe constitué par
 - (a) faire passer ledit air à travers un récipient contenant du carbone actif,
 - (b) traiter ledit air avec du charbon actif,
 - (c) traiter ledit air avec de la silice,
 - (d) traiter ledit air avec une résine adsorbant les composés aromatiques,
 - (e) soumettre ledit air à un procédé d'hydrogénéation,
 - (f) extraction dudit air avec un hydrocarbure aliphatique liquide, et
 - (g) soumettre ledit air à un procédé d'oxydation.
4. Procédé selon la revendication 1, dans lequel ledit hydrocarbure est choisi dans le groupe constitué par le méthane,

l'éthane et le propane, et dans lequel ladite zone réactionnelle chauffée fonctionne à une température de 300°C à 600°C.

5. Procédé selon la revendication 1, dans lequel ledit hydrocarbure est choisi dans le groupe constitué par l'éthylène, l'acétylène, le propylène et le méthylacétylène, et dans lequel ladite zone réactionnelle chauffée fonctionne à une température de 150°C à 300°C.
6. Procédé selon la revendication 1, dans lequel ledit hydrocarbure est l'éthylène.

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